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# NANOCOMPOSITES OF METALLOPHthalOCYANINES AND CONJUGATED POLYMERS

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## ABSTRACT

Nanocomposites of phenoxy-substituted vanadyl phthalocyanine with a  $\pi$ -conjugated polymer, poly(benzimidazobenzophenanthroline ladder), have been prepared from their Lewis acid complexes in organic solvents. The resulting composite thin films obtained by spin-coating have excellent optical transparency and interesting composition-dependent morphology and photoelectronic properties. Enhanced photoconductivity, compared to the components, was observed in some composites with discrete nanoscale metallophthalocyanine aggregates.

## INTRODUCTION

Organic materials, such as metallophthalocyanines (MPc), squaraines, perylenes, and azo compounds, are of interests for applications in photoelectronic devices. Among these materials, metallophthalocyanines are most attractive because of their broad spectral responses and high photosensitivities.<sup>1</sup> For instance, pigments of titanylphthalocyanine have been reported to have one of the best photosensitivities ( $0.2 \mu\text{J}/\text{cm}^2$ ) among organic photoconductors.<sup>2</sup> However, because most unsubstituted metallophthalocyanines have poor processibility as a result of their very limited solubility, organic photoconductors are usually prepared by dispersing fine particles of metallophthalocyanine pigments in an insulating polymer matrix.<sup>3</sup> The pigment particles, after wet milling, typically have sizes of several hundred nanometers in diameter.<sup>4</sup>

Since the inert polymer matrix is not photoactive nor charge-transporting, it may contain traps that impede charge transport.<sup>5</sup> The use of active polymer matrix may improve the performance of photoconductors. Moreover, there is interest in new photoconductors with sensitivity over a wide spectral range, i.e., with photosensitivity in both the visible and the near-IR region.<sup>6</sup> Approaches to such materials include the combination of pigments with similar or dissimilar structures,<sup>6</sup> and the dispersion of pigment particles in a photoconductive polymer matrix.<sup>5</sup>

Nanoscale size effects on the photoconductivity of nanocomposites and conjugated polymers were recently reported.<sup>7,8</sup> Here, we report the preparation and the photoconductive properties of novel nanocomposites consisting of tetraphenoxy-substituted vanadyl phthalocyanine (VOTPPc) and a conjugated polymer, poly(benzimidazobenzophenanthroline ladder)(BBL) (Figure 1). Our measurements show that some of the composites have an enhanced quantum efficiency of photogeneration and photosensitivity when the dispersed VOTPPc phase is in the nanoscale size range.

## EXPERIMENTAL SECTION

**Materials.** The polymer BBL with an intrinsic viscosity of 32 dL/g in methanesulfonic acid at 30°C was synthesized in this laboratory, using the literature method.<sup>9</sup> Nitromethane (~96%), Gallium (III) chloride ( $\text{GaCl}_3$ , ~99.999%), and vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine (VOTPPc, ~98%) were obtained from Aldrich and were used as received. Binary composites of VOTPPc/BBL with VOTPPc content of 10%, 25%, 50% and 75% molar fraction were prepared by dissolving the two components in nitromethane containing  $\text{GaCl}_3$  in a vial. All the solutions were prepared in  $\text{N}_2$  atmosphere dry box. In general, a composite solution contains 0.2-0.4wt% solids. The viscous solutions of all the composites investigated were readily processed into thin films on various substrates (glass, fused silica) by solution spin-coating. Thin films of the composites were prepared by spin coating and the complexed  $\text{GaCl}_3$  in the thin films was removed by submerging them in deionized water for 4 hours.<sup>10</sup>

**Characterization.** Optical absorption spectra were obtained with a Perkin-Elmer Model Lambda 9 UV-Vis spectrophotometer. Photoinduced discharge experiments were performed by mounting a bilayer photoreceptor device in a xerographic cycling chamber. The bilayer photoreceptors were composed of a thin layer of composite as the charge generation layer and a thick layer of tri-p-tolylamine (TTA) doped polycarbonate as charge transport layer. The detail methods for device fabrication and evaluation have been discussed elsewhere.<sup>8</sup> For transmission electron microscopy (TEM), the composite thin films on glass substrate were placed in deionized water, peeled off using a blade, and transferred onto copper grids. The TEM images were obtained from a JOEL model JEM2000EX instrument. All measurements were made at room temperature (~22°C).

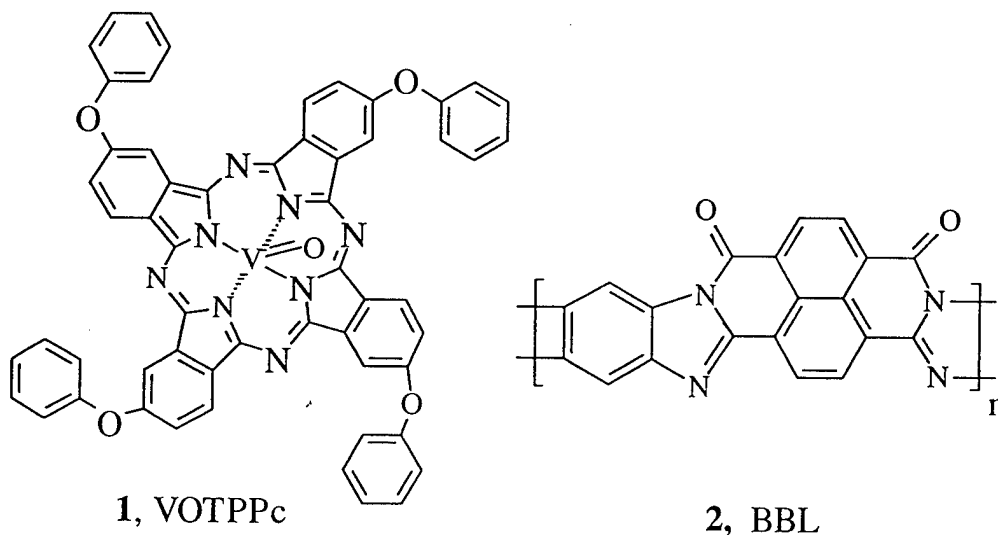


Figure 1. Molecular structures of VOTPPc and BBL

## RESULTS AND DISCUSSION

We have exploited the solubility of metallophthalocyanines and conjugated polymers in the same organic solvent to prepare composites of various metallophthalocyanines with different

conjugated polymers. We have found that the metallophthalocyanines, such as VOTPPc, H<sub>2</sub>Pc, CuPc, and TiOPc, have good solubility in aprotic organic solvents containing metal halide Lewis acids (e.g. GaCl<sub>3</sub>). The high solubility of the metallophthalocyanines in these solvents is due to their complex formation with Lewis acids at the imine nitrogen sites, similar to the aromatic heterocyclic rigid-rod polymers.<sup>10</sup>

Transmission electron micrographs of the composite thin films showed that VOTPPc molecules formed aggregates in the conjugated polymer matrix (Figure 2). Thin films of pure BBL were structureless, even at higher TEM resolution. The aggregation of VOTPPc molecules in the composites shows that BBL and VOTPPc are thermodynamically incompatible, as expected from the huge disparity in molecular weight and structure. The size of the VOTPPc aggregates was found to depend on the composition. Isolated nanoscale MPc domains with sizes of ~ 10 nm were observed at low MPc concentration (10% VOTPPc) whereas a largely bicontinuous morphology was observed at higher loading of the metallophthalocyanine (50-75%). At intermediate composition (25%), the composite morphology contains both continuous and isolated domains of the VOTPPc.

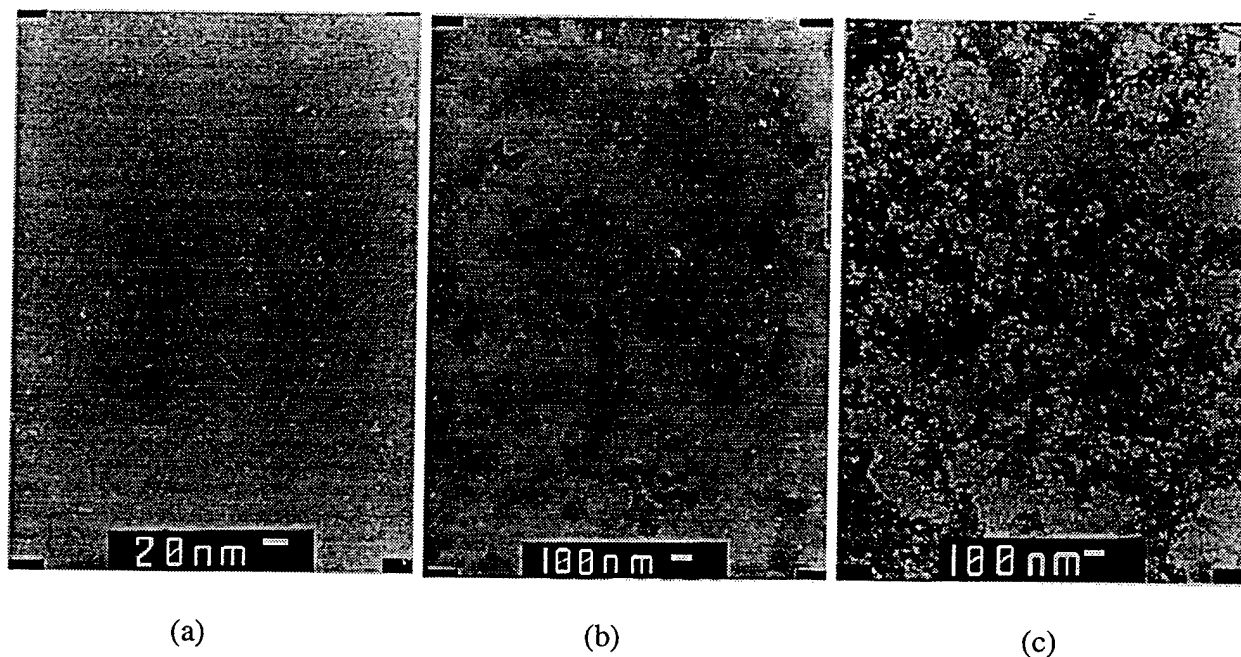


Figure 2. Transmission electron micrographs of VOTPPc/BBL composites: (a) 10%; (b) 25%; and (c) 50% VOTPPc

Thin films of the VOTPPc/BBL composites had excellent optical transparency and their color varied depending on the VOTPPc content. As the VOTPPc content varied from 10-75%, the color changed from purple to blue to blue green to green. Figure 3 shows the optical absorption spectra of BBL and the VOTPPc/BBL composite thin films on fused silica substrates. The absorption spectra of the composites were simple compositional averages of those of the pure components. The composites showed absorption bands with  $\lambda_{\text{max}}$  at 645 and 720 nm which are characteristic of VOTPPc. Vanadyl phthalocyanine (VOPc) pigment is known to have three different polymorphs: phase I, II, and III.<sup>11</sup> Only phase II has absorption in the near-IR region with  $\lambda_{\text{max}}$  around 840 nm, whereas neither phase I nor phase II shows any IR absorption. By

comparison with the absorption spectra of the polymorphs of VOPc<sup>11</sup> and t-BuVOPc (phases I and II),<sup>12</sup> we assign the absorptions of the composites at 645 and 720 nm as those of phase I of VOTPPc. Thus, it appears that VOTPPc aggregated primarily in a non-IR absorbing glassy form (phase I) under the spin-coating conditions. Phase I of vanadyl phthalocyanine, substituted or unsubstituted, is metastable and transforms to phase II by heating<sup>11</sup> or by treating with solvent vapor.<sup>12</sup> Our differential scanning calorimetry measurement shows that this phase transformation for VOTPPc starts at 200°C. Thus, all the results presented in this paper are for the phase I polymorph of VOTPPc.

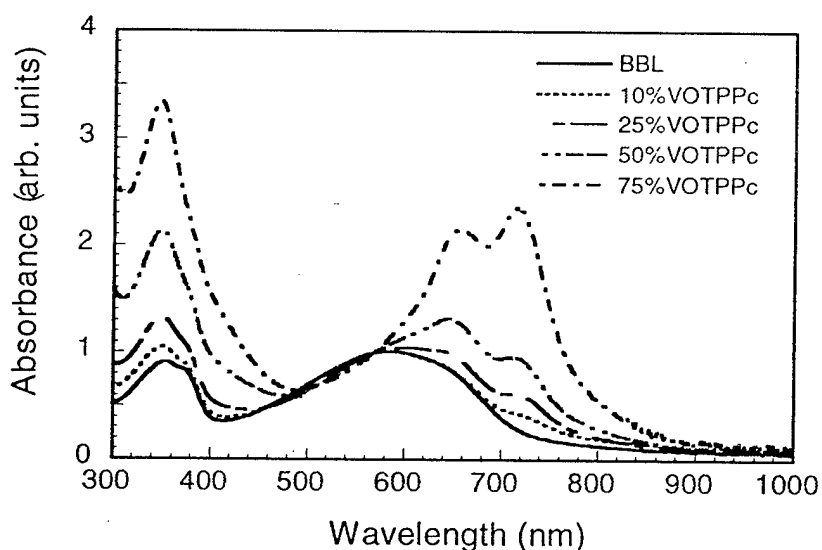


Figure 3. UV-Vis absorption spectra of VOTPPc/BBL composites.

The photoconductivity of the composites was characterized by the photoinduced discharge method.<sup>13</sup> A bilayer device was used with a charge generation layer of 50-nm thick VOTPPc/BBL composite and a 16- $\mu$ m thick TTA:polycarbonate charge transport layer. The photoinduced discharge curves for the pure components and the VOTPPc/BBL composites are shown in Figure 4. The result for the pure VOTPPc (Figure 4a) in which no difference was observed between dark decay and upon light exposure indicates that phase I aggregates of VOTPPc are not photoactive, in agreement with prior observations on other vanadyl phthalocyanines.<sup>14</sup> The reason why phase I polymorph of VOPc is not photoactive whereas phase II is remains unclear but is speculated to be related to the orientation of V=O bonds in an aggregate.<sup>14</sup> Unidirectional orientation of V=O is believed to enhance intermolecular interactions, favoring efficient charge carrier photogeneration in an ordered crystalline pigment. As observed in t-BuVOPc,<sup>14</sup> disordered orientation of V=O in amorphous aggregates appears to inhibit charge carrier photogeneration.

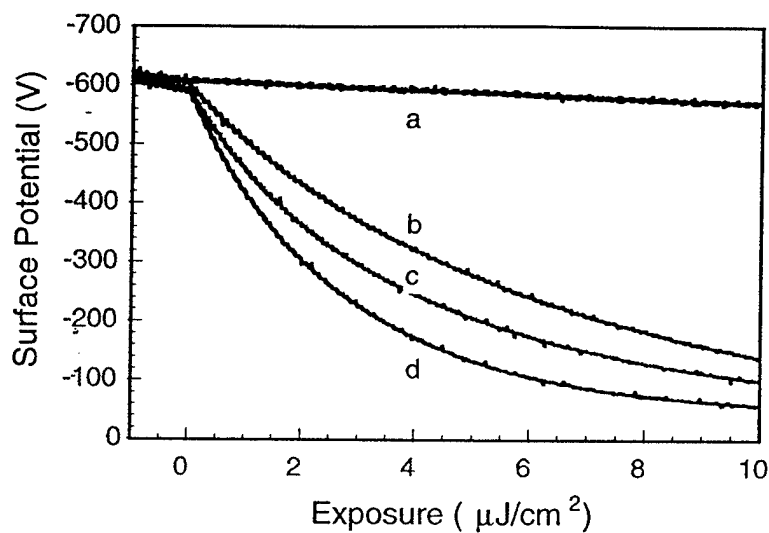


Figure 4. Photoinduced discharge curves of VOTPPc/BBL composite photoreceptors under 570 nm illumination: (a) pure VOTPPc (100%), (b) 25%VOTPPc, (c) pure BBL (0%), and (d) 10%VOTPPc.

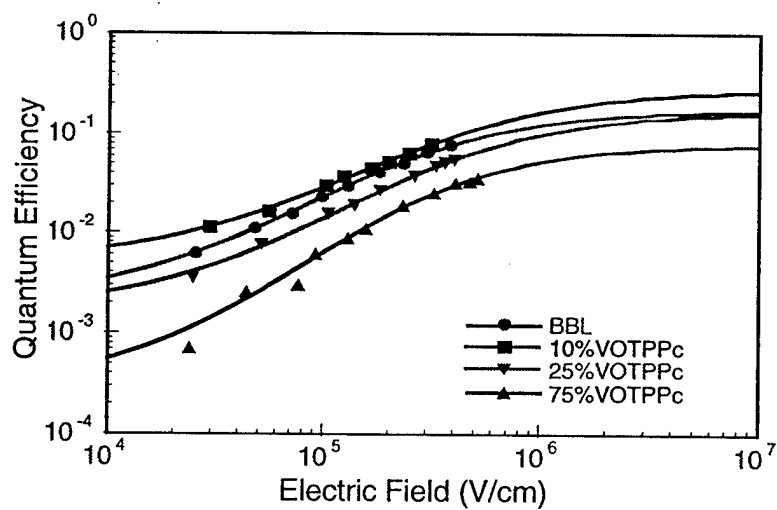


Figure 5. Electric-field dependence of photogeneration quantum efficiency of VOTPPc/BBL composites under 570 nm illumination.

All the VOTPPc/BBL composites were photoactive with photosensitivity that varied with composition (Figure 4). The 10% VOTPPc composite has the best photosensitivity,  $1.9 \mu\text{J}/\text{cm}^2$ , which is significantly better than pure BBL ( $2.8 \mu\text{J}/\text{cm}^2$ ). The electric field-dependent quantum efficiency for charge photogeneration in pure BBL and three composites is shown in Figure 5. The results show that the 10% composite has enhanced photoconductivity compared to BBL, the matrix material. The main correlation between morphology and the photoelectronic properties of these composites is that enhanced photoconductivity (photosensitivity, charge photogeneration efficiency) is only observed in the composite with discrete nanoscale aggregates of VOTPPc dispersed in the conjugated polymer matrix. Similar nanoscale size effects on photoconductivity of  $\text{BiI}_3$ -nylon nanocomposites<sup>7</sup> and layered conjugated polymers<sup>8</sup> have been reported. The physical origin of the nanoscale enhancement of photoconductivity in the latter case was elucidated in terms of the *interface-mediated charge separation* and the *small exciton diffusion lengths* in the materials.<sup>8</sup> These mechanisms appear to be the likely explanation of our observed enhancement of photoconductivity in VOTPPc/BBL composites at 10%. However, additional studies are necessary to establish this.

## CONCLUSIONS

The solubility of the Lewis acid complexes of metallophthalocyanines and  $\pi$ -conjugated polymers in a common organic solvent has allowed us to prepare well-defined supramolecular materials which combine the electroactive and photoactive properties of both components. The resulting composites have excellent optical transparency, composition-dependent morphology, and enhanced photoconductivity.

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